Treatment and Biogas Production of Sulfate Containing Low-Strength Industrial Wastewater in Upflow Anaerobic Sludge Blanket (UASB) Reactors

	リク　ユキキン
氏　　名	陸　　雪琴
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指　導　教　員	東北大学教授　李　玉友
論文審査委員	主査　東北大学教授　李　玉友
	東北大学教授　西村　修　東北大学准教授　久保田 健吾
	東北大学准教授　坂巻 隆史

論 文 内 容 要 旨

To deal with the wastewater-related environmental issues, among the multifarious alternatives, the Upflow Anaerobic Sludge Blanket（UASB) reactor is by far one of the most widely adopted anaerobic options for treatment of various wastewaters due to its high efficiency, flexibility, energy generation in the form of biogas and low sludge production. However, when UASB treatment is applied to high-strength sulfate containing wastewater, the competition between sulfate reducing bacteria (SRB) and methane producing archaea (MPA) to utilize the carbon sources often leads to a decrease in the methane production and even failure of the treatment process. Consequently, it is very important to well understand the interaction between SRB and MPA.

Therefore, the purpose of my research was to enhance the technical feasibility of the UASB process in the treatment of low-strength industrial wastewater with high concentration of sulfate and simultaneous bioenergy recovery, advancing the applications of the technology in water industry from basic science. Long-term performance of UASB reactor in treating two kinds of synthetic wastewaters containing starch and methanol were evaluated.

The whole thesis consisted of 7 chapters along with acknowledgement and publications. The whole thesis structure is illustrated in Fig. 1. In Chapter 1, it introduced the background of industry wastewater discharge and global energy crisis; meanwhile, the objectives of the thesis were also described. In Chapter 2, we provided a literature review on recently developed technologies for industrial wastewater treatment. The Chapters 3 to 6 were the main part of the research for the thesis. In Chapter 7, the important conclusions were obtained based on the experimental results from this study. Besides, recommendations for further investigation were given as well.

The studies were conducted step by step from 2013 to now, with the following outcomes to be achieved.

(1) To evaluate the long-term performance of UASB reactor in starch wastewater treatment. A lab-scale UASB reactor has been constructed and operated for more than 200 days to comprehensively evaluate the long-term performance of the reactor in treating starch wastewater. The effects of organic loading rates (OLR) on the overall stability were examined by varying hydraulic retention times (HRT) (from 24 to 3 h) to optimize the operating condition. In order to elucidate the responsible pathway for starch biodegradation, the specific methanogenic activity (SMA) of granules by feeding seven different substrates were also determined. Besides, the possible changes of water qualities (i.e. pH, ORP, COD, acetate, etc.) and granule characteristics (i.e. morphological and microbial structure, EPS distribution, settling velocity, etc.) along the reactor height were detected, hoping to map the core degradation dynamics occurred in the interior of UASB.

(2) To understand how the COD/SO_4^{2-} ratio affects the biodegradation routes of starch wastewater as well as subsequent methane production and

sulfate reduction. The balance of COD and sulfate conversion under different scenarios were calculated to explore the relative portion of electron donor transferred into MPA and SRB. Activity tests were performed to clearly explore the biodegradation kinetics of starch. Furthermore, morphological and microbial structures of granular sludge were characterized by scanning electron microscopy (SEM) and fluorescence in situ hybridization (FISH). Finally, the energy conversion efficiencies of the reactor under different COD/SO_4^{2-} ratios were calculated, with the purpose of providing more basic data and theoretical guidance for advancing its practical application.

(3) To assess the long-term performance of UASB reactor in treating methanolic wastewater and to in-depth explore the granulation/dispersion mechanisms of granular sludge. The effects of OLR on the overall stability were investigated by varying HRT from 48 to 2 h to optimize the operating conditions. The granule characteristics including morphological and microbial structure, extracellular polymeric substances (EPS) distribution and metal cations (Ca^{2+}, Mg^{2+}, Fe^{2+}, K^{+}, and Na^{+}) in different EPS fractions, and specific methane activities (SMAs) were researched, aiming to thoroughly elucidate the core methanol degradation dynamics occurred in the interior of UASB.

(4) To assess the introduction of sulfate with different COD/SO_4^{2-} ratios on the long-term performance of UASB reactor in treating methanolic wastewater by taking the performance, granulation and microbial community into account. Meanwhile, it also intended to gain deeper insight into the competitive and syntrophic interactions between the different bacterial trophic groups in the reactor, and to inspect and verify whether the dispersed sludge could be re-granulated or not if the sulfate was introduced. The reactor has been run continuously under mesophilic condition for around 235 days. The effects of sulfate on the overall stability were investigated by varying the influent COD/SO_4^{2-} ratio from 20 to 0.5 to optimize the conditions, and the granule characteristics (e.g. EPS, metal cations, and metabolic activity) as well as microbial community were discussed as well.

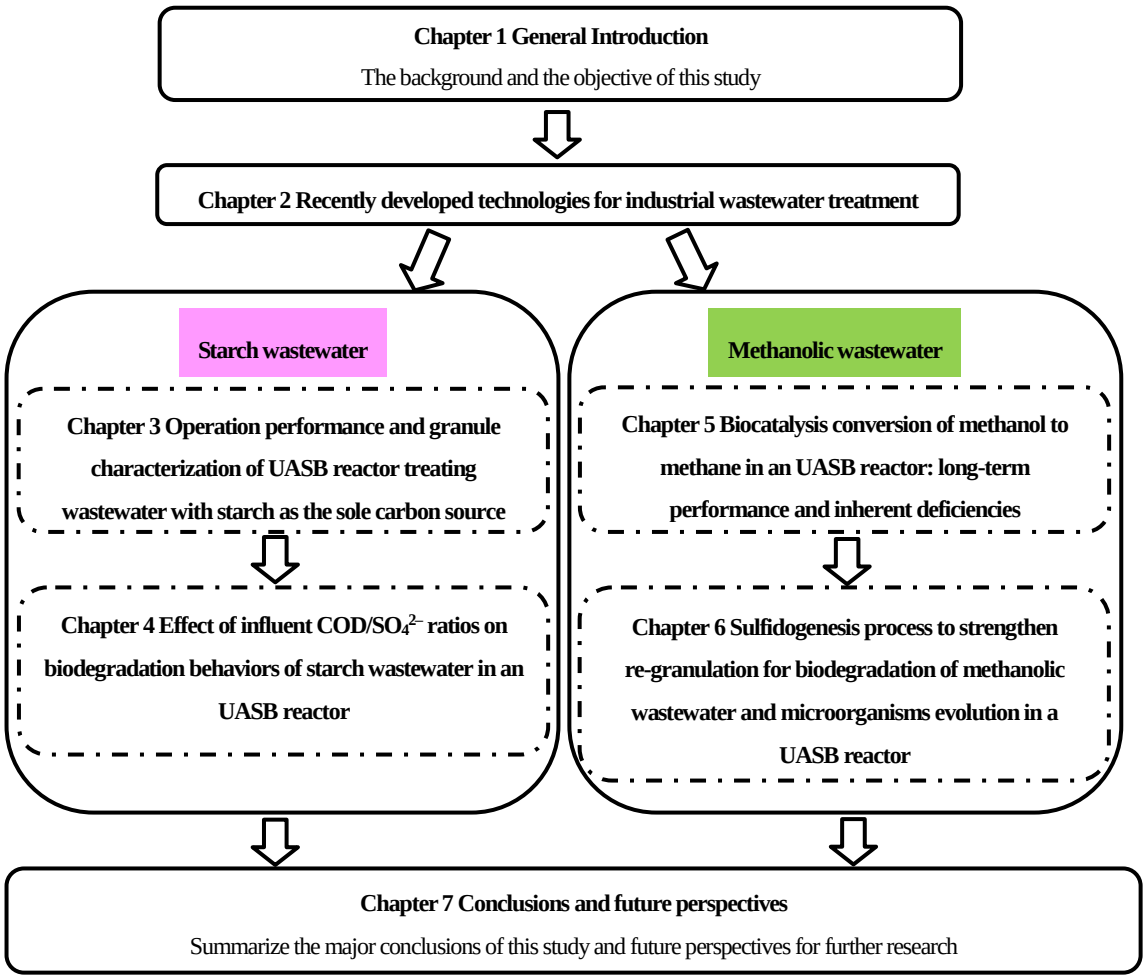

Figure 1 The whole thesis structure.

Fig. 2 shows the research routes of my doctor thesis. In general, this thesis can be divided into three parts: first, the effects of OLR on the overall stability were examined by varying HRT to optimize the operating condition; second, the core degradation dynamics occurred in the interior of UASB was analyzed; third, the influent COD/SO_4^{2-} ratios were optimized to promote the organic and sulfate removals as well as bioenergy production. My work would provide preliminary basis and theoretical guidance for the practical applications of UASB technology in the real world.

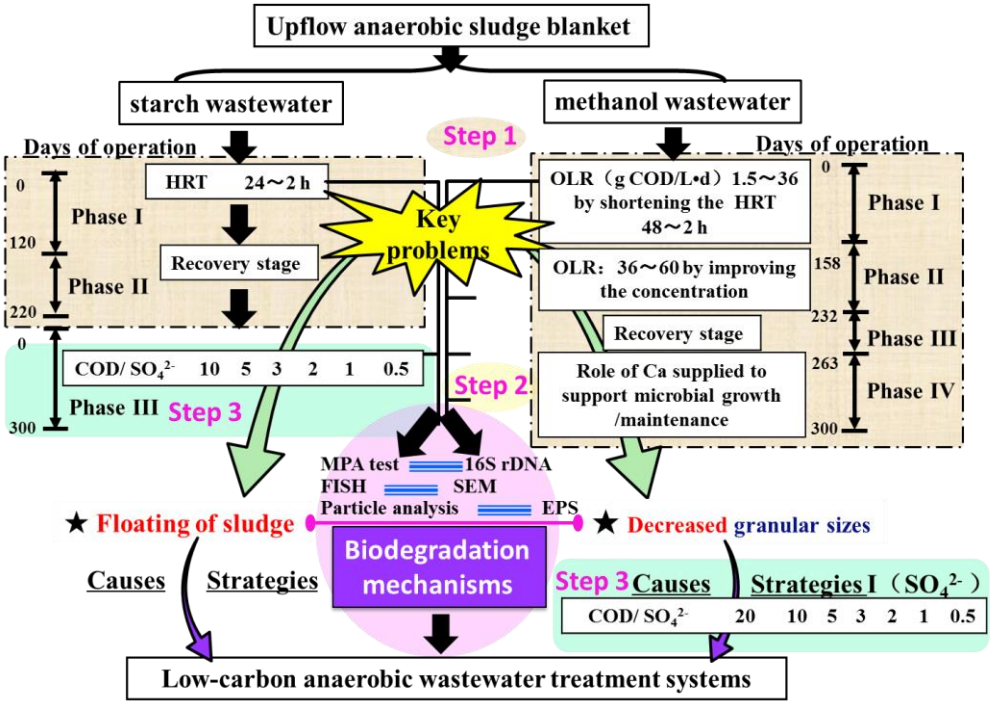

Figure 2 Research routes of the doctor thesis.

The long-term performances of UASB reactors in treatment and chemical energy harvest from low-strength industrial starch and methanolic wastewater were investigated systematically under different operational conditions (i.e. OLR, HRT, influent COD/SO_4^{2-} ratios, etc.). The main outcomes obtained in this thesis are as follows:

(1) The long-term performance of a lab-scale UASB reactor treating starch wastewater was investigated under different HRT. Successful start-up could be achieved after 15 days' operation. The optimal HRT was 6 h with OLR 4 g COD/L·d at COD concentration 1000 mg/L, attaining 81.1–98.7% total COD removal with methane production rate of 0.33 L CH_4/g $COD_{removed}$. Specific methane activity tests demonstrated that methane formation via H_2-CO_2 and acetate was the principal degradation pathways. Vertical characterizations revealed that main reactions including starch hydrolysis, acidification and methanogenesis occurred at the lower part of reactor ("main reaction zone"); comparatively, at the up converting acetate into methane predominated ("substrate-shortage zone"). Further reducing HRT to 3 h caused volatile fatty acids accumulation, sludge floating and performance deterioration. Sludge floating was ascribed to the excess polysaccharides in extracellular polymeric substances (EPS). More efforts are required to overcome sludge floating-related issues.

(2) A lab-scale UASB has been run for 250 days to investigate the influence of influent COD/SO_4^{2-} ratios on the biodegradation behavior of starch wastewater and process performance. Stepwise decreasing COD/SO_4^{2-} ratio enhanced sulfidogenesis, complicating starch degradation routes and improving process stability. The reactor exhibited satisfactory performance at a wide COD/SO_4^{2-} range ≥ 2, attaining stable biogas production of 1.15–1.17 L/L·d with efficient simultaneous removal of total COD (73.5–80.3%) and sulfate (82.6 ± 6.4%). Adding sulfate favored sulfidogenesis process and diversified microbial community, invoking hydrolysis-acidification of starch and propionate degradation and subsequent acetoclastic methanogenesis; whereas excessively enhanced sulfidogenesis (COD/SO_4^{2-} ratios <2) would suppress methanogenesis through electrons competition and sulfide inhibition, deteriorating methane conversion. This research in-depth elucidated the role of sulfidogenesis in bioenergy recovery and sulfate

removal, advancing the applications of UASB technology in water industry from basic science.

(3) The long-term performance of methanol biocatalysis conversion in a lab-scale UASB reactor was evaluated. Properties of granules were traced to examine the impact of methanol on granulation. Methanolic wastewater could be stably treated during initial 240 d with the highest biogas yield of 18.6 ± 5.7 L/L·d at OLR 48 g-COD/L·d. However, the reactor subsequently showed severe granule disintegration, inducing granule washout and process upsets. Some steps (e.g. increasing influent Ca^{2+} concentration, etc.) were taken to prevent rising dispersion, but no clear improvement was observed. Further characterizations in granules revealed that several biotic/abiotic factors all caused the dispersion: (1) depletion of EPS and imbalance of protein/polysaccharide ratio in EPS; (2) restricted formation of hard core and weak Ca-EPS bridge effect due to insufficient calcium supply; and (3) simplification of species with the methanol acclimation. More efforts are required to solve the technical deficiencies observed in methanolic wastewater treatment.

(4) The effect of sulfidogenesis process on sludge granulation was studied. The beneficial sulfidogenesis process invoked the significant increase in Fe iron and more EPS secretion that bound and immobilized in the sludge, which inspired the sludge re-granulation. The UASB reactor maintained the satisfactory performance at a wide COD/SO_4^{2-} range of ≥ 2, attaining high biogas production of 3.78 ± 0.32 L/L·d with efficient concurrent removal of total COD (96.54 ± 4.39%) and sulfate (56.34 ± 12.99%). Methane content in biogas kept a fairly stable level of 81.5 ± 1.6% at all COD/SO_4^{2-} ratios tested. Particle size of granules showed that a clear increase in the particle size as decreasing the COD/SO_4^{2-} ratios. Despite that the enhanced sulfidogenesis led to electron flow distributed into the SRB (20.00 ± 2.43%), but MPA (80.00 ± 2.43%) could out-compete sulfate reducers even at low COD/SO_4^{2-} ratio of 0.5 in organics removal and electrons utilization. Activity tests and microorganism results of low COD/SO_4^{2-} ratio suggested that the conversion of methanol into methane is not only depend on the less acetoclastic methanogen and hydrogenotrophic methanogenesis, but also depend on incomplete oxidizer SRB species (*Desulfovibrio* sp.) utilized H_2/CO_2 with acetate to achieve mineralize the methanol to methane. In consequence, the metabolic pathway of methanol was diversified. Further analysis through SEM, FISH and microorganism shift revealed that lower COD/SO_4^{2-} ratio favored sulfidogenesis process, diversified the microbial community and complicated metabolic pathway of methanol inside the reactor. The benefical sulfidogenesis process subsequently revealed that several biotic/abiotic factors all benefit the re-granulation: (i) form the EPS network due to sufficient Fe-EPS bridge; (ii) enhance microbial diversity by incomplete oxidizer SRB species (*Desulfovibrio* sp.) utilized H_2/CO_2 with acetate to achieve mineralize the methanol to methane; and (iii) complicate metabolic pathways of methanol, which was vital driving force to the sludge re-granulation. This research verified the favorable effect of sulfidogenesis in strengthening re-granulation and bioenergy recovery for biodegradation of methanolic wastewater, providing the fundamental data and theoretical guidance for advancing the widespread applications of UASB technology in water industry from basic science.

UASB has showed great operation performance in treating synthetic industrial wastewater during the thesis. As a consequence, it is every suitable for the industrial wastewater treatment due to its numerous advantages such as higher up-flow velocity, low energy consumption, low sludge production, higher removal efficiency, vast potential of resource recovery, less equipment required and high operational simplicity.

論文審査結果の要旨

近年、循環型社会構築の観点から、バイオエネルギーが注目されている。廃水処理の分野においてはUASB法などの嫌気性生物処理は省エネルギー・創エネルギーがあるので、その応用拡大が期待されている。本研究は製紙および化学産業で多く発生するメタノール系・でんぷん系の硫酸塩を含む廃水へのUASB法の適用可能性について実験的に検討した。本論文は以下の通り7章から構成される。

第1章は「緒論」であり、本研究の背景、研究の目的、意義についてまとめ、本論文の構成について述べた。

第2章「既往の研究現状および研究課題」では、まず産業廃水処理技術の開発に関する既往研究をまとめた。次に、硫酸塩を含むでんぷん系およびメタノール系廃水処理技術の嫌気性処理に関する研究動向について考察した。最後、本研究の位置づけを定め、研究課題を抽出した。

第3章ではUASBプロセスによる低濃度でんぷん系廃水の処理性能を評価した。でんぷんを含む低濃度（COD:1g/L）人工廃水を用いてHRTを24hから3hまで変化させた連続実験を行い，UASB処理性能に及ぼすHRTの影響を評価した。HRT3~12 hの条件において流入CODの60~80%がメタンガスに変換されたが、HRT6hでのバイオガス回収率は78.6%であり、最も高かった。またでんぷん系廃水処理におけるグラニュールの肥大化・枝化現象を把握し、その原因を考察した。

第4章では硫酸塩を含むでんぷん系廃水のUASB処理に及ぼすCOD/SO_4^{2-}比の影響について検討した。HRTを6hに設定して硫酸塩濃度を100mg/Lから2000mg/Lまで（COD/SO_4^{2-}比が10から0.5まで）変化させてUASB処理の連続実験を行い、メタン生成と硫酸塩還元などの処理性能を把握した。また各COD/SO_4^{2-}比での電子流れを計算し、COD/SO_4^{2-}比が2以上の条件ではメタン生成が主反応であるのに対してCOD/SO_4^{2-}比が1以下の条件では硫酸塩還元が支配的な反応になることを示した。

第5章ではメタノールを唯一の炭素源とする（COD:3 g/L）人工廃水を用いて長期連続運転を行い、UASBリアクターの安定性と運転特性を評価したとともに、グラニュール微細化の原因を解析した。COD除去率を90%以上に維持するための処理負荷の限界は48 g-COD/L/d程度であった。また、メタノール系廃水処理におけるグラニュールの微細化原因は微生物群集の単一化に伴い、汚泥中のEPS濃度が著しく低下したためであると考えられる。

第6章では硫酸塩を含むメタノール系廃水のUASB処理に及ぼすCOD/SO_4^{2-}比の影響について検討するため、メタノールを唯一の炭素源として（COD:3 g/L)、硫酸塩濃度を150mg/Lから6000mg/Lまで（COD/SO_4^{2-}比が20から0.5まで）変化させてUASB処理の連続実験を行い、各COD/SO_4^{2-}比での電子流れや物質収支を把握したとともに、硫酸含有条件下におけるメタノールの嫌気性分解経路と微生物群集構造を解析した。COD/SO_4^{2-}比が0.5になってもメタン生成が依然として主反応であった。また、硫酸塩の存在は嫌気性処理に悪影響を与えず、むしろ微生物群集構造の変化によりグラニュールの形成が大きく改善されたことが示された。

第7章では本研究を通して得られた結果を総括し、今後の展望について述べている。

以上、要するに、本論文は従来嫌気性処理が適さないとされてきた低COD・高硫酸塩系廃水のUASB処理を試み、製紙産業や化学産業でよく見られるメタノール系廃水とでんぷん系廃水について長期的連続実験を行い、処理水質、メタン回収およびメタン生成と硫酸塩還元の競合と微生物群集構造の変化など多岐にわたり総合的解析を行った。その成果は排水浄化システムの構築と設計に重要な知見を与え、環境工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。